Standard Operating Procedure
for the Analysis of Metals in Waters and Wastewaters
by ICP Method 200.7
Using the Perkin Elmer Optima 4300 DV and 5300 DV

United States Environmental Protection Agency
Region 5 Central Regional Laboratory
536 South Clark Street (ML-10C)
Chicago, Illinois 60605

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Primary Analyst: 050608

Group Leader: 6 May 08

Quality Assurance Coordinator: 5/6/08

CRL Deputy Director: 5/6/2008

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1. SCOPE AND APPLICATION

1.1. This Standard Operating Procedure (SOP) is applicable to the analyses of twenty-nine elements in waters and wastewaters using CRL digestion procedure Metals025 (200.2 Hotblock method). Other digestion methods may be used, such as Metals033, which is a beaker digestion, but is rarely used. The analysis method is based on 200.7, which is approved for NPDES monitoring in 40 CFR part 136.3, Table 1B for 25 of these elements. Twelve of these are priority pollutants per 40 CFR part 401.15. Of the 25, 21 of them are reported routinely by CRL, as well as three other unregulated elements. The other four may be reported if present in sufficient amount. Other subsets of these may be reported for various programs based on the Data Quality Objectives (DQOs) of the project. At the CRL, as a matter of routine, As, Se, Sb and Tl are reported by Graphite Furnace Atomic Absorption (GFAA) instead of ICP. The sensitivity of this method allows these elements to be reported by ICP depending on the DQOs of the project, for example, for TCLP extracts.

1.2. The instruments used for the analysis of metals by ICP as described here are the Perkin Elmer Optima 4300 DV and 5300 DV, using both an axial and radial view of the plasma.

1.3. The elements determined by this SOP include the following:

Analyte	Symbol	Registry Number (CASRN) Chemical Abstract Services	P.P.*	Table IB
Aluminum	Al	7429-90-5		✔
Antimony	Sb	7440-36-0	✔	✔
Arsenic	As	7440-38-2	✔	✔
Barium	Ba	7440-39-3		✔
Beryllium	Be	7440-41-7	✔	✔
Boron	B	7440-42-8		✔
Cadmium	Cd	7440-43-9	✔	✔
Calcium	Ca	7440-70-2		✔
Cerium	Ce	7440-45-1		
Chromium	Cr	7440-47-3	✔	✔
Cobalt	Co	7440-48-4		✔

Analyte	Symbol	Registry Number (CASRN) Chemical Abstract Services	P.P.*	Table IB
Copper	Cu	7440-50-8	✔	✔
Iron	Fe	7439-89-6		✔
Lead	Pb	7439-92-1	✔	✔
Lithium	Li	7439-93-2		
Magnesium	Mg	7439-95-4		✔
Manganese	Mn	7439-96-5		✔
Molybdenum	Mo	7439-98-7		✔
Nickel	Ni	7440-02-0	✔	✔
Potassium	K	7440-09-7		✔
Selenium	Se	7782-49-2	✔	✔
Silver	Ag	7440-22-4	✔	✔
Sodium	Na	7440-23-5		✔
Strontium	Sr	7440-24-6		
Thallium	Tl	7440-28-0	✔	✔
Tin	Sn	7440-31-5		✔
Titanium	Ti	7440-32-6		
Vanadium	V	7440-62-2		✔
Zinc	Zn	7440-66-6	✔	✔

*P.P. refers to Priority Pollutant listing in 40 CFR part 401.15. Table IB refers to 200.7 being an allowable method under 40 CFR part 136, Table IB. Cerium is included due to its potential for spectral interferences.

1.4. The Method Detection Limits (MDLs), Reporting Limits (RLs), Linear Dynamic Ranges (LDRs) and calibration ranges are found in Appendix A.

1.5. The laboratory uncertainty, at the 95% confidence interval, for this method is expressed in Appendix B as a percentage window about the concentration of the spiked blank. This uncertainty will vary by analyte, will be greater near the reporting limit and will be much greater near the MDL. Usually, the sampling component of the uncertainty will be far greater than the laboratory uncertainty.

1.6. Samples with silver values greater than 0.1 mg/L in the digest will be redigested after dilution and reanalyzed, due to the 0.5% HCl concentration in the 200.2 digestion. The solubility of silver is dependent on the formation of the $[AgCl_2]^-$ complex.

1.7. This method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation. Such samples may be prepared with multiple dilutions prior to digestion to obtain a more accurate barium result.

1.8. If reporting between the MDL and the reporting level is requested, the results will be rounded to one significant figure.

1.9. For elements having a high channel and a low channel, the high channel is used when the sample exceeds the standard of the low channel.

1.10. Dissolved samples are prepared just as are the corresponding total samples to insure proper matrix matching. It is recommended that both are analyzed together.

2. SAFETY AND WASTE HANDLING

2.1. Toxicity or carcinogenicity of reagents used in this SOP has not been fully established. Each chemical should be considered as a potential health hazard and individual exposure should be minimized. Standard safety practices are to be followed such as the wearing of personal protective wear (safety glasses, gloves, lab coats) and referring to available MSD sheets. Follow the rules detailed in the Region 5 Central Regional Laboratory Health, Safety, and Environmental Compliance Manual and the Toxic Substance safety plans.

2.2. Radiation sources - intense ultra violet (UV) and radio frequency (RF) - are present when operating the ICP-OES spectrometer. Reasonable precautions to avoid exposure to these emitted radiation sources should be taken. This would include not looking directly at the ignited plasma or its reflection. The 4300 DV and 5300 DV are equipped with interlocks on the torch compartment door that will not allow the plasma to be ignited if the door is ajar. Unless routine maintenance is required in the torch compartment, the door should always be closed.

2.3. Within the spectrometer, lethal high voltages are present. Routine maintenance that would require the analyst to access high voltage areas should not be performed on the instrument unless the instrument is powered down and locked and tagged out. The instruments are covered by service contracts and only trained, professional service engineers should perform complex repairs (i.e. non-routine) maintenance.

2.4. For instrument waste collection, the usual 5 gallon waste carboy is used in place of the one supplied with the ICP. This eliminates the step to transfer liquids when the container becomes full.

2.5. Unused portions of stock solutions, acids, calibration and analytical standard solutions, nebulizer waste and digested samples must be poured into the RED labeled waste containers. The used sample tubes are single-rinsed and disposed of in yellow hazardous waste bags.

3. DEFINITIONS

3.1. Axial: End-on plasma viewing; i.e. spectrometer looks down the central channel of the plasma and collects analyte emission over the length of the plasma.

3.2. DQO: Data Quality Objective

3.3. DUP: Duplicate

3.4. DV: Patented Dual View system used in the Perkin Elmer Optima ICP-OES spectrometers which employs a software-controlled mirror to allow plasma to be viewed either radially or axially.

3.5. ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometer

3.6. IEC: Interelement Corrections

3.7. LCB: Laboratory Control Blank

3.8. LCM: Laboratory Control Solution Measured

3.9. LCS Laboratory Control Standard

3.10. LD: Laboratory Duplicate

3.11. LIMS: Laboratory Information Management System

3.12. Linearity: The range for which data behaves in linear manner

3.13. LRB: Laboratory Reagent Blank

3.14. LSF: Laboratory Spike Fortified

3.15. MDL: Method Detection Limit

3.16. MS: Matrix Spike

3.17. NPDES: National Pollutant Discharge Elimination System

3.18. QAPP: Quality Assurance Project Plan

3.19. QMP: Quality Management Plan

3.20. Radial: Side-on plasma viewing; i.e. the spectrometer views the analyte emission from the side of the plasma.

3.21. RCRA: Resource Conservation and Recovery Act

3.22. RF Radio Frequency

3.23. RL: Report Level

3.24. RLC: Report Level Check

3.25. RPD: Relative Percent Difference

3.26. SIC: Spectral Interference Checks

3.27. Subarray: A subsection of the patented Perkin Elmer SCD (Segmented-array Charge-coupled Device) detector, which consists of a group of pixels (a unit of array detector whose output can be read individually) on an array detector which are positioned to measure a small, specific wavelength range.

3.28. Super Q: Laboratory distilled water is passed through a mixed bed resin column before use.

3.29. TCLP: Toxicity Characteristic Leaching Procedure

4. SUMMARY OF METHOD

4.1. This method describes the determination of 29 elements dissolved and stabilized in aqueous acidic media which are then analyzed by the use of an ICP-OES unit, namely the Perkin Elmer Optima 4300 DV or 5300 DV. As a matter of routine, representative sample sub-aliquots (50 mL for waters) are taken and digested with mineral acids using CRL block digestion procedures or beaker/hot plate digestion procedures using mineral acids. These digestion procedures are designed to insure that as much of the analytes that are available for recovery (i.e. total recoverable) are rendered soluble and relatively stable in aqueous acidic medium.

> Please note: For description of the digestion methods see SOP METALS025 hot block digestion or METALS033 CLP-type beaker digestion. It is noted that the acid strength of the standards in this method are matched only by digestion method METALS025 hot block digestion.

4.2. The resulting solutions are peristaltically pumped and pneumatically aspirated into aerosol mists which are conveyed in an argon gas stream through an inductively RF coupled region whereby a plasma is formed. Within the plasma, final desolvation, ionization, excitation and characteristic radiative emission for the analytes take place. The resultant emitted radiation is directed through the optics of the spectrometer where it is dispersed via a grating into component wavelengths that are indicative of specific elements present in the plasma. The intensity of the characteristic radiation is measured using a Charge- Coupled solid-state Detector (CCD).

4.3. The plasma can be viewed radially (from the side) and axially (down the central channel). If sample concentrations are expected to be low, axial, with a longer path length, will yield greater sensitivity. If concentrations are expected to be high, radial views will extend the linear range to greater concentrations. Since most elements have multiple analytical lines in this method, some were chosen to have one or more lines with axial view for sensitivity, but with a line viewed radially to extend the concentration range. The major elements are all viewed radially, because low concentrations of these elements were not needed for environmental decision-making.

4.4. The Perkin Elmer Optima ICP optics are purged with argon, which is always used when conducting an analysis with this analysis method. MgF_2 optics along with the argon gas purge facilitate the measuring of analyte lines in the far UV portion of the electromagnetic region of the spectrum. Emission intensities are counted at analyte peak locations and compared to counts obtained from calibration standards containing known amounts of specific analytes. The sample concentration values are calculated via the Perkin Elmer ICP WinLab software, typically using first order regression analysis calculations. For a given spectral line, one to three pixels of the detector are used to define the area under the peak. This integrated intensity is corrected for interferences by means of an Inter-Elemental Correction (IEC) model.

4.5. The concentration results and the integrated data are printed out. Integrations are variable length based upon intensity at the subarray. The average of several integrations is used for the reported value.

5. CAUTIONS

5.1. Potassium, due to ionization enhancement effects, is biased high by 10 to 20% in a typical sample with 50-100 mg Na/L. This effect has been mitigated by the use of the rubidium internal standard. The effects on other easily ionizable elements is still under study.

5.2. To increase instrument stability, hoods in the room where instrument is located, in addition to hoods in the adjoining laboratory, should be closed.

5.3. For best performance, monitor the intensities of the internal standard for both axial and radial measurements. The intensities are affected by the condition of the purge windows, as well as the sample delivery system.

5.4. If high suspended solids are apparent in the samples, the samples should be prepared with dilutions prior to analysis as well as analyzing directly.

5.5. High dissolved solids can contribute to salting out on the tip of the nebulizer and this will affect plasma performance. If high dissolved solids are suspected in the samples, monitor the nebulizer and take corrective action if necessary.

6. SAMPLE HANDLING AND PRESERVATION

6.1. All samples must have been collected using an approved and appropriate sampling plan.

6.2. Samples should be collected in polyethylene bottles with solid polypropylene caps. It is recommended that the bottles be pre-treated. The bottles may be soaked for twenty four hours with dilute nitric acid before use. The usual contaminants have been found to be lead and zinc. At least 200 mL of sample is requested to allow a duplicate and spike to be analyzed. More would be necessary if reanalyses were needed.

6.3. Water samples are preserved in the field to a pH<2. Use 5 mL of 1:1 HNO_3 per liter of sample or blank. More acid may be used if necessary.

6.3.1. If the sample is not acidified for any reason, especially due to an anticipated hazard, an indication of this condition should accompany the samples and be directed to the attention of the Metals Group Leader. If pH is > 2, either the pH must be adjusted with HNO_3 and time allowed to re-solubilize the analyte(s) that may have adsorbed onto the container walls (24 hr. minimum), or if the sample is extremely basic or highly buffered, and addition of acid would cause precipitation of the analytes of interest, this fact and the pH of the sample must be documented.

6.4. Samples can be held for six months prior to analysis.

6.5. Field filtered (dissolved metals) samples are digested and treated the same as total metals samples.

7. INTERFERENCES

7.1. Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra. A certain amount of background is intrinsic to the plasma source itself. One component of this background is black-body radiation, which is the light emitted by any heated body. Another component is Bremsstrahlung, which results from

collisions of the accelerated electrons and charged particles. The third component of the light emitted from the plasma itself is cyclotron radiation. This is the result of electrons being accelerated in a magnetic field, and is much stronger near the work coil. The sum of these effects is a broad emission band with the maximum at about 460 nm.

7.2. An important contribution to the background of the plasma is the result of reactions between components of the sample matrix or surrounding atmosphere. Nitrogen and oxygen combine in the envelope around the plasma to give excited NO molecules which emit a structured spectrum from about 180 to 230 nm. Water from the sample gives rise to OH emission, mostly in the 280 to 310 nm region. NH occurs about 360 nm; CO gives background from 180-200 nm; CN has spectra from 388 to 420 nm.

7.3. Another source of continuum background is the reaction of excited atoms from the sample with atmospheric oxygen. An example of this is the AlO emission from the oxygen cutoff (approx 180 nm to 230 nm).

7.4. Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak.

7.5. Line spectra are a very rich source of interference in plasma emission spectroscopy. Every component of the sample emits to some degree, and even the argon itself has a number of emission lines. Of the latter, only one channel (Na588.995) has a serious argon line interference.

7.5.1. Line spectral interferences can be grossly classified into two categories: overlapping lines, either through direct coincidence or within the resolving power of the instrument, and broadened lines. Directly overlapping lines of comparable strength are relatively rare, the appearance of the strong lines for Cd at 228.80 nm and As at 228.81 nm being an exception. More often, the analyte line is very near to a line from a major constituent, such as the Be 234.86 nm line which is within about twice the full width at half maximum (FWHM) of the Fe line at 234.81 nm.

7.5.2. Emission lines of elements have an intrinsic natural line width which is quite narrow, resulting in the large number of significant figures found in wavelength tables. The plasma is a very complex system; these lines are broadened by a number of means. Doppler broadening results from the distribution of velocities of the emitting particles in the hot environment of the plasma. Collisional broadening takes many forms, from Van der Waals broadening by collision with neutral argon atoms, Stark broadening by collision of electrons with ions, and resonance broadening. The latter form of line broadening is most important when the interfering element is at high concentration. If an element has two lines which are close enough to be in resonance, and is present at high concentrations, collisions of the form

$$X^*_1 + X_g \text{ ---> } X_g + X^*_2$$

can take place, where X_g refers to ground state X and X^*_1 and X^*_2 are the two resonance excited states. The Al lines gain a significant background from the Ca lines which are well separated at low levels.

7.6. Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by the use of Inter-Element Correction (IEC) equations. Interelement correction is a spectral interference correction technique in which emission contributions from interfering elements that emit at the analyte wavelength are subtracted from the apparent analyte emission after measuring the interfering element concentrations at other wavelengths.

7.7. Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they may be ameliorated by use of an internal standard. Yttrium is the most common choice of internal standard. If it is used, the same amount must be added to all standards and samples. Both ICPs are equipped with a second peristaltic pump to be used for addition of the internal standard.

7.8. If high suspended solids are apparent in the samples, the samples should be prepared with dilutions prior to analysis as well as analyzing directly.

7.9. High dissolved solids can contribute to salting out on the tip of the nebulizer and this will affect plasma performance. If high dissolved solids are suspected in the samples, monitor the nebulizer and take corrective action if necessary.

7.10. Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-OES technique. The most common interference of this type can be seen in the analysis of an alkali metal (*e.g.* K) in the presence of a high concentration of another alkali metal (*e.g.* Na). Alkali metals are easily ionized, but are determined by emission from the neutral species.

7.10.1. A high concentration of one will supply an excess of electrons to the plasma, boosting the neutral atom population of the less concentrated alkali metal, causing an enhancement relative to the standards.

Please note: This phenomena was studied during method development on the Perkin Elmer 3300 DV. The studies showed that those elements that are being determined axially are not affected. However, the transition elements that are determined radially, will be affected in a highly alkali matrix.

Please note: The effect of sodium and potassium on each other has been mitigated by the use of the rubidium internal standard. The effects on other easily ionizable elements is still under study.

7.11. Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system thoroughly between samples.

8. APPARATUS

8.1. Perkin-Elmer Optima 4300 DV or 5300 DV Inductively coupled argon plasma atomic emission spectrometer with 32-bit software, equipped with:

8.1.1. Polyscience refrigerated recirculator or equivalent,

8.1.2. Perkin Elmer AS93 autosampler or equivalent,

8.1.3. Perkin Elmer peristaltic sample pump or equivalent,

8.1.4. Gilson peristaltic Internal Standard pump or equivalent,

8.1.5. GemCone (Conespray) nebulizer or equivalent,

8.1.6. Cyclonic spray chamber or equivalent, and

8.1.7. Dell Optiplex GX270 computer, Dell monitor, Hewlett Packard LaserJet 4050 (or equivalent) or equivalent.

8.2. Argon Supply (GP55 Liquid)

8.3. Volumetric flasks, Class A glass, (100 mL ± 0.2 mL) and Class B polypropylene (100 mL ± 0.2 mL)

8.4. Volumetric Pipets, Class A, 10, 5, 1 mL ± 1%

8.5. 30 mL polystyrene cups

8.6. 50 mL centrifuge tubes

8.7. Eppendorf pipets and tips. Eppendorf pipets are certified quarterly. Results are kept in log book in ICP laboratory.

9. REAGENTS AND STANDARDS

9.1. Nitric Acid: Ultrex , Baker Instra-Analyzed or GFS Chemicals redistilled or equivalent. Each lot received is assigned a LIMS ID. Expiration date is five years from receipt.

9.2. Hydrochloric Acid: Ultrex, Baker Instra-Analyzed or equivalent. Each lot received is assigned a LIMS ID. Expiration date is five years from receipt.

9.3.Concentrated nitric and hydrochloric acids may be found in LIMS under UNASSIGNED, because any group may use them.

9.4.Nitric acid (1+1) -- Add 250 mL conc. nitric acid to 200 mL of ASTM Type I water and dilute to 0.5 L. Solution expires after one year.

9.5.Hydrochloric acid (1+1) -- Add 250 mL conc. hydrochloric acid to 200 mL of ASTM Type I water and dilute to 0.5 L. Solution expires after one year.

9.6. Water: Laboratory distilled water is passed through a mixed bed resin column before use. The water is called "Super Q", named after a column once used. All water used for ICP analysis and standards is Super Q.

9.7. 2% HNO_3 wash solution: In a 1-liter volumetric flask, 20 mL HNO_3 is added to Super Q water.

9.8. Triton-X 100 wash solution (2% HNO_3, 0.1% Triton-X 100): In a 1-liter volumetric flask, 20 mL HNO_3 and 1 mL Triton-X 100 is added to Super Q water.

Please note: Sonication will speed dissolution of the Triton-X 100.

9.9. Plasma-grade certified 1000 mg/L standards: These standards must be of sufficient purity that mixing standards will not result in addition of unknown amounts of other elements, possibly affecting the final concentration of the analyte. For this reason High-Purity Standards and Spex Standards or equivalent are recommended for mixed standards. Each standard is entered into LIMS upon its arrival. The expiration date by convention is the end of the month given by the vendor, unless a specific date is given.

9.10. All calibration and analytical standard preparations must be documented in LIMS. All solution bottles shall be properly labeled with the LIMS information. The expiration date for all such working solutions is one year from the date of preparation. Separate standards/solutions and separate preparation records must be maintained by the ESAT staff.

9.11. For simplicity when entering a new instance of a standard that is already in LIMS, select one that is already made, then click on Copy. Then the relevant information is updated. Check that Solvent/Solvent Lot contains the acid matrix, usually 1% HNO3

0.5% HCl. Enter the LIMS IDs of acids used. Maintain a current list of standards by pruning expired ones. At this point, remove at least one expired standard by editing the Department fields to read Expired Standards. If an expired standard is the only one of it's type, retain the standard in the list so that others may have the convenience of copying the record when preparing it again.

9.12. To create a label with LIMS, click Print, then click Standard Labels. A Print Standard Labels box will pop up; use the dropdown box to select the "lst_m@5160.rpt" print format, designed for label sheets sized as Avery 5160. Avery 5162 Weatherproof labels stick well, even on moist surfaces, and do not fade. Select the standard to print with either the magnifying-glass icon or the menu dropdown button. Click the Preview button, input the number of copies to print, and the number of labels to skip. If you feed the printer a partially-used label sheet and enter the number of used locations, printing will begin at the next available place. When the print preview screen appears, click Print Options -> Printer Setup and select Manual Feed. Manual feed has the printer bypass the main paper tray, and instead print on a blank label sheet that you will load, face up, into manual feed tray. Before, or shortly after pressing the Print icon, load the label sheet into the manual feed tray. This will print information required by NELAC: standard name, LIMS ID number, preparation and expiration dates, and analyst name. For compliance with our safety policy, the acid matrix is also printed. LIMS can print just one standard label at a time, but Promium will improve upon this in the future. Here is an example label:

ICP (w) LCM 1

Expires Apr-10-08 7101001

By Greg Mitsakopoulos Nov-08-07

1% HNO3 0.5% HCl

9.13. A uniform system of naming standards makes them simple to sort on the Description column in the Metals Standards screen, and allows for labeling consistency. The naming convention for standards and solutions is based on technique, matrix, standard. It is suggested that standards be named according to the Standard ID column in the preparation tables below.

9.14. The following table outlines the standards used for calibrating the instrument. The standards are prepared from VHG Labs EPA Methods Standards (or equivalent):

Standard ID	Stock ID	Element(s)	Stock Conc. (mg/L)	Final Conc. (mg/L)
ICP (w) CAL BLANK			0	0
ICP (w) CAL 1	VHG Labs 44CS1Y-100	Ca K Mg P As Se Tl Zn B Ba Be Cd Ce Co Cr Cu Mn Ni Pb Sr V Ag*	1,000 500 200 50	10 5 2 0.5
ICP (w) CAL 2	VHG Labs 44CS2Z-100	Al Fe Mo Na SiO_2 Ti Sb Li Sn	1,000 500 200	10 5 2
ICP (w) CAL 3: Ag/Pb	High Purity	Ag‡ Pb	1 1,000	0.1 10
ICP (w) CAL HI	High Purity	Al Ca Fe Mg K Na	10,000 10,000	500 200

*Present in the standard, but not currently used for calibration

‡Silver in the Ag/Pb standard (ICP (w) Ag int for CAL 3) is made from a 1.00 mg/L Ag intermediate which is made from diluting 0.1 mL of 1000 mg/L Ag stock into a 100 mL volumetric containing 10 mL of 1:1 HCl. This intermediate is stable in the 5% HCl matrix.

Please note: Calibration standards are prepared in 100 mL volumetric flasks. Add 50 mL Super Q, 1 mL 1:1 HCl, and 2 mL 1:1 HNO_3 to each flask. Add the required volume of stock standard(s) and bring to volume. Transfer the working standard to the designated 125 mL Nalgene calibration standard bottle. During analysis, the calibration standards are transferred to 50 mL centrifuge tubes placed in the autosampler. Standards in use may be left in the centrifuge tubes. The Cal Blank is the exception, being made fresh in a polypropylene volumetric flask. This is to avoid introducing contaminants in the calibration blank, particularly zinc, possibly biasing subsequent results low.

Please note: When preparing standards, always transfer the stock standards to a fresh 30 mL polystyrene cup to avoid contamination. Never pipet directly from a stock standard bottle. Always close the bottle immediately after pouring to maintain the stock standard concentration. Do not leave standards or acids in the polystyrene cups for extended periods of time, as they will pick up contaminants such as zinc.

9.15. The traceability of both the single-element standards and the Inorganic Ventures Environmental Solutions (or equivalent) is given on the Certificate of Analysis sheet that is provided by the manufacturer. This certificate is kept in a ring binder in the ICP laboratory (room 1025).

9.16. The following table outlines the analytical standards used during the course of an analytical run. The standards are prepared from a second source, separate from the source used to prepare the calibration standards, Inorganic Ventures Environmental Solutions (or equivalent):

Standard ID	Stock ID	Element(s)	Stock Conc. (mg/L)	Final Conc. (mg/L)
ICP (w) LCB			0	0
ICP (w) LCM 1	Inorganic Ventures QCP-QCS-1	K* P SiO_2 Sn* Tl	500	5
		As Hg* Pb Sb	200	2
	QCP-QCS-2	Al B Ba Be Ca Cd Ce Co Cr Cu Fe Li Mg Mn Mo Na Ni Sr Ti V Zn	100	1
		Ag*	25	0.25
ICP (w) LCM 2: Ag/Sn	High Purity brand Spex	Sn	500	1
		Ag†	1	0.05
ICP (w) LCM HI	Inorganic Ventures EPA-V-3C	Al Ca Fe K Na	1000	100
		Mg	600	60

*Present in the standard but not used in this standard for QC purposes

†Silver in the LCM 2 standard (ICP (w) Ag int. for LCM 2) is made from a 1.00 mg/L Ag intermediate which is made from diluting 0.1 mL of 1000 mg/L Ag stock (Spex for second source) into a 100 mL volumetric containing 10 mL of 1:1 HCl. This intermediate is stable in the 5% HCl matrix.

Please note: Analytical standards are prepared in 200 mL volumetric flasks. Add 100 mL Super Q, 2 mL 1:1 HCl, and 4 mL 1:1 HNO_3 to each flask. Add the required volume of stock standard(s) and bring to volume. Transfer the working standard to the designated 250 mL Nalgene analytical standard bottle. The LCB is made in a polyethylene volumetric flask. Try preparing LCM1, LCM2 and HiLCM at 200 mL or 500 mL at a time, at your discretion, since there are at least two AQC sets per run., and calibration standards are made 100 mL at a time.

Please note: When preparing standards, always transfer the stock standards to a fresh 30 mL polystyrene cup to avoid contamination. See the note in section 9.6.

9.17. The following table outlines the Reporting Limit Check (RLC) stock standards. The standard is prepared from High Purity Environmental Solutions (or equivalent). Two

stock solutions are made so that the 100 mL polypropylene flasks may be used. The two solutions are combined in one 100 mL polypropylene flask:

Stock solution #1 (add 1 mL to 100 mL for working RLC):

Element	RLC Stock Conc. (μg/L)	High Purity(HP) Stock Conc. (mg/L)	Vol. HP Stock Used (mL)	Final Vol. (mL)	Working RLC Conc. (μg/L)
Ag	500	1,000	0.05	100	5.0

Stock solution #2 (add 0.2 mL to 100 mL for working RLC):

Element	RLC Stock Conc. (μg/L)	High Purity(HP) Stock Conc. (mg/L)	Vol. HP Stock Used (mL)	Final Vol. (mL)	Working RLC Conc. (μg/L)
Al	50,000	10,000	0.5	100	100
As	10,000	1,000	1.0	⇓	20
B	25,000	1,000	2.5	⇓	50
Ba	1,500	1,000	0.15	⇓	3.0
Be	500	1,000	0.05	⇓	1.0
Ca	100,000	10,000	1.0	⇓	200
Cd	1,000	1,000	0.1	⇓	2.0
Co	1,500	1,000	0.15	⇓	3.0
Cr	2,500	1,000	0.25	⇓	5.0
Cu	2,500	1,000	0.25	⇓	5.0
Fe	25,000	10,000	0.25	⇓	50
K	40,000	10,000	4.0	⇓	800
Li	12,500	1,000	1.25	⇓	25
Mg	50,000	10,000	0.5	⇓	100
Mn	500	1,000	0.05	⇓	1.0
Mo	2,000	1,000	0.2	⇓	4.0
Na	200,000	10,000	2.0	⇓	400
Ni	1,500	1,000	0.15	⇓	3.0
Pb	7,500	1,000	0.75	⇓	15
Sb	10,000	1,000	1.0	⇓	20
Se	15,000	1,000	1.5	⇓	30
Sn	5,000	1,000	0.5	⇓	10
Sr	1,000	1,000	0.1	⇓	2.0
Ti	2,500	1,000	0.25	⇓	5.0
Tl	10,000	1,000	1.0	⇓	20
V	2,500	1,000	0.25	⇓	5.0

Element	RLC Stock Conc. (μg/L)	High Purity(HP) Stock Conc. (mg/L)	Vol. HP Stock Used (mL)	Final Vol. (mL)	Working RLC Conc. (μg/L)
Zn	15,000	1,000	1.5	⇓	30

9.18. The following table outlines the Spectral Interference Check (SIC) standards. These standards must be analyzed at least once each analysis day directly following instrument calibration. The components of these standards were chosen based on spectral evidence found during method development which points to possible areas of weakness in the interference correction models. The analyst must fill-out the SIC standard log (located at the instrument) every time the standards are analyzed. The standards are prepared from High Purity Environmental Solutions (or equivalent):

SIC SOLUTION	ELEMENT(S)	CONCENTRATION	ACID MATRIX
ICP(w) SIC 1: Co/V	Co, V	10 mg/L	1% HNO_3 0.5% HCl
ICP (w) SIC 2: Ce	Ce	10 mg/L	1% HNO_3 0.5% HCl
ICP (w) SIC 3: Cr/Mo	Cr, Mo	10 mg/L	1% HNO_3 0.5% HCl
ICP (w) SIC 4: Cu/Ti	Cu, Ti	10 mg/L	1% HNO_3 0.5% HCl
ICP (w) SIC 5: Fe/Mn	Fe, Mn	Fe: 300 mg/L Mn: 10 mg/L	1% HNO_3 0.5% HCl
ICP (w) SIC 6: Al	Al	200 mg/L	1% HNO_3 0.5% HCl
ICP (w) SIC 7: Ca	Ca	200 mg/L	1% HNO_3 0.5% HCl
ICP (w) SIC 8: Mg	Mg	200 mg/L	1% HNO_3 0.5% HCl

Please note: The SIC standards are prepared in 100 mL volumetric flasks. Add 50 mL Super Q, 1 mL 1:1 HCl, and 2 mL 1:1 HNO_3 to the flask. Add the appropriate

amount of the concentrated stock(s) to the flask. For example, for 10 mg/L, add 1 mL of 1000 mg/L to the flask. For 300 mg Fe/L, add 3 mL of 10000 mg Fe/L stock to the flask. These solutions are valid for one year from preparation.

9.19. The following table outlines Spike Solution A and B. These solutions are added to the sample designated for matrix QC audits at the time of digestion. The solutions are prepared from High Purity Environmental Solutions (or equivalent):

Spike Solution	Elements	Stock Conc. (mg/L)	Amount Added (mL)	Final Conc. (mg/L)*
A	Be	0.5	1	0.01
	Ag	1.25		0.025
	Cd	2.5		0.05
	Co Cr Cu Li Mo Ti V	5		0.1
	As Ba Mn Ni	10		0.2
	Ce Pb Sb Se Sn Tl	25		0.5
B	Al B Fe Sr Zn	50	1	1
	Mg	1000		20
	K	1250		25
	Ca Na	2500		50

*of analyte in digestate.

Please note: Spiking solutions A and B are prepared in 1000 mL and 200 mL volumetric flasks, respectively. Add 20 mL Super Q to each volumetric flask. Add 50 mL Conc. HCl to the 1000 mL volumetric, and 10 mL Conc. HCL to the 200 mL volumetric. Add the required volume of stock standard(s) and bring to volume. The High Purity stock standard concentrations are all 1000 mg/L for spiking solution A. The High Purity stock standard solutions are all 10,000 mg/L for spiking solution B. Transfer each spiking solution to the designated 1000 mL spiking solution bottle. The stock spike soluions expire one year from preparation.

Please note: When preparing the spiking solutions, always transfer the stock standards to a fresh 30 mL polystyrene cup to avoid contamination. See note in 9.6.

Please note: When making Spike B, be careful not to initially add too much water otherwise, you will run out of room in the flask before completely adding all of it's component standards.

9.20. Should a consistent bias be discovered in a standard, usually by comparison to a second source, a third source (usually NIST) is employed to determine which is more correct. The vendor(s) are contacted to negotiate a replacement, or the vendor is changed.

9.21. Yttrium/Rubidium internal standard (ICP ISTD: Rb/Y) : Add 2.5 mL of 10,000 mg/L Y stock standard and 5 mL of 10,000 mg/L Rb stock standard to a 500 mL volumetric flask to which has been added 10 mL 1:1 HNO_3 and 5 mL 1:1 HCl. After bringing the flask to volume with Super-Q water, this is then transferred to a 500 mL Nalgene bottle for storage and is dispensed to a 250 mL Nalgene bottle with holes to receive tubing. The same 500 mL flask is reused for this purpose only. This solution is valid for six months, but will be used up before that time.

Please note: If preferred, the internal standard solution can be made up a liter at a time.

9.22. In LIMS, maintain a current list of standards by pruning expired ones. Remove at least one expired standard by editing the Department fields to read Expired Standards. If an expired standard is the only one of it's type, retain the standard in the list so that others may have the convenience of copying the record when preparing it again.

10. **PROCEDURE**

10.1. Power up the computer and log in. Engage the pump tubing on both the sample peristaltic pump and the internal standard peristaltic pump, making sure that the pump tubing tension arm is fully engaged on all tubes. If the pump tubing is new, stretch the tubing several times by grasping the tubing on the ends and pulling gently.

Please note: It is recommended that the hood sash be kept in a lowered position while the plasma is on, as the canopy is operating on the same fan. If manipulations must be performed in the hood while the plasma is on, the sash should be returned to the lowered position as soon as possible after completion of the task.

Please note: The ICP is run with the spray chamber compartment door open to help equilibrate temperature.

10.2. Fill the wash water reservoir with Triton-X 100 wash solution (2% HNO_3, 0.1% Triton-X 100) if dirty samples are expected. If samples are clean, Super Q water or 2% HNO_3 may be used. Place the internal standard line in the yttrium/rubidium internal standard reservoir.

10.3. Check argon supply. Check chiller (Temperature should be set at 16°C).

10.4. Enter ICP WinLab32 software. Open the current water method file. This method will be labeled as **water_mmddyy**, where mmddyy is a date with month, day, and year.

> Please note: The Method Editor window can be opened to see (and edit) method parameters. However, changes to the method may **not** be saved without approval of the Metals Group Leader. If the method is changed, with approval from the Metals Group Leader, save the modified method to a different name, and enter the document changes in the instrument log book.

10.5. Open the Plasma Control window; click the toggle switch in the window to begin plasma ignition sequence. Once the plasma has been successfully ignited, observe plasma through viewing window to ensure plasma is stable. Allow at least an hour for the plasma to stabilize before beginning the run. Have the probe in the wash solution and the internal standard pump running at least one-half hour before analysis begins.

10.6. If the analyst has a Work Space saved, open it now by going to File on the tool bar, then Open and then Work Space (It is recommended that the analyst save his or her own Work Space on the system).

> Please note: The save Work Space option of the software allows the analyst to save a series of windows that are open on the screen and are routinely used during the course of an analysis (i.e. Results window, Automated Analysis Control window, Spectra window, etc...). It also saves information like Results file, Sample Information file and Method. The analyst **must use caution** when opening his or her Work Space to insure that the correct method is being used and that the results are being saved to the appropriate results file.

10.7. Open the Sample Information Editor to create a Sample Information file. Enter the information that is common to all samples (e.g. the Batch Number, Analyst, sample batch description, etc...). Then, enter the information that is specific to each sample (e.g. A/S Location, Sample ID, Dilution and Analyze QC Before fields). By clicking **New** after entering the Sample Information Editor, the analyst may select a template for the .sif file. In the Administrator folder, there is a water template with all the desired fields.

> Please note: Analytical QC are queued within the method to run automatically at certain times during the course of the analytical run (i.e. after the initial calibration and at the end of the run). Use the Method Editor window to see when the analytical QC are queued to run automatically. If all or some of the QC standards must be run additional times during the analytical run, the QC standards must be identified in the "Analyze QC Before" field.

10.8. After creating the Sample Information File, save it using the current date as the file name (use the following convention: MMDDYY.sif, where MM is the two digit month, DD is the two digit day, and YY is the two digit year). Goto the Set-UP page in the Automated Analysis Control window and specify the Results file name by clicking on the

Browse button. Enter a file name using the same naming convention as used for the Sample Information file (a brief description of the results file can also be entered here). Enter the Sample Information file name created earlier. Load the autosampler. An aid in this is the Autosampler Loading List, which may be found under **System**. Fresh calibration blank and LCB are made each day, as trace amounts of contaminants, such as zinc accumulate in the 50 mL centrifuge tubes over time. The amount picked up is not sufficient to affect the concentration of the calibration standards, however.

10.9. On the Set-Up page of the Automated Analysis Control window, click the box next to Hg Realign. This will trigger a Hg realignment to be performed at the beginning of the analysis (the Hg Realign must be performed at least once per analysis run).

Please note: If the analyst has saved his or her Work Space and the Hg Realign box has been checked in the Automated Analysis Control window before saving the Work Space, the Hg Realign box will remain checked every time the Work Space is opened and a Hg realignment will be performed automatically at the beginning of the automated analysis.

10.10. On the Analyze page of the Automated Analysis Control window review the sequence of the standards and samples to be run in the "sequence pane."

Please note: The analytical sequence will not mirror what was entered in the Sample Information Editor. The calibration standards and automated QC's will appear in the sequence pane, but will not be entered by the analyst in the Sample Information Editor. Calibration standards and automated QC's are entered in the Method Editor series of windows.

10.11. A typical analytical sequence is as follows:

10.11.1. Instrument calibration standards

10.11.2. Quality control standards (i.e. LCB, LCM1, LCM2, LCMHI and Reporting Limit Check standard).

Please note: High concentration check standards (*e.g.* LCMHI) should be followed by at least one blank wash sample to minimize carryover.

10.11.3. RLC and SIC solutions, generally followed by the periodic check standards.

10.11.4. Series of sample digests (10 or fewer) including digested QC, spike blanks, LCS (if necessary) and matrix duplicates & spikes.

10.11.5. Periodic quality control check standards (again, the LCB, LCM1, LCM2 and LCMHI).

10.11.6. Another group of ten samples or less, if present, and periodic quality control check standards until finished.

10.11.7. Final quality control check standards (i.e. LCB, LCM1, LCM2 and LCMHI) are analyzed at the end after all the samples and digestion QC.

Please note: If changes are made to either the automated QC's in the Method Editor window or the samples/standards in the Sample Information Editor, the Rebuild List button on the Analyze page in the Automated Analysis Control window must be clicked to update the sequence pane.

10.12. After reviewing the analytical sequence click on the **Analyze All** button on the Analyze page of the Automated Analysis Control window. This will initiate an analysis run in which all calibration standards, samples and QC standards will be run. It is possible to analyze the calibration standards separately by choosing the **Calib** button, but normally one will use **Analyze All**. No samples may be analyzed before calibration standards have been run that day.

Please note: The method currently does not have pass/fail criteria triggered to have the instrument automatically perform certain tasks should a QC standard fail to meet the pass criteria. The analyst must therefore monitor the status of the analysis to ensure that all the QC audits are successful (i.e. within the control limits for the specific QC audit).

10.13. When running high and low level samples together, be alert for memory effects. The Triton-X 100 solution reduces memory effects considerably. However, carryover may still be a problem with some samples. If carryover is detected, stop the automated analysis by clicking on the Analyze All button once again and follow the appropriate instructions on the pop-up window that appears. Allow the system to flush completely with the Triton-X 100 wash solution. Once complete, continue the analysis at the point where it was interrupted. If high samples are suspected, a wash may be inserted into the .sif file.

10.14. When running total and dissolved samples in pairs, it is best to analyze them one after the other. In this way, slight biases of a few percent in the calibration checks are reflected in both results, and make the comparison of the two results easier.

10.15. When the analysis is finished, replace the wash and the yttrium/rubidium internal standard solution with laboratory distilled water. Flush water through the system for 5 to 10 minutes while the plasma is still on. When this is complete, turn off plasma by clicking on the "on/off" toggle switch on the Plasma Control Window.

10.16. It is noted that the method is set of run with the spectrometer purge gas on High. High purge gas flow helps keep the optical compartment free of air, which assists in the measurement of analytes with shorter wavelengths. However, the software does not

change the purge gas flow to Normal on shutdown. Setting the purge gas to normal after the run is complete but before shutdown will conserve Ar while the instrument is on standby (not being used for analyses). To do so, select Spectrometer Control and use the radio button to select normal purge gas flow. Click OK.

10.17. Disengage sample and internal standard pump tubing and release the tension on the tubing. Shut down the ICP WinLab32 software.

10.18. Data should be uploaded to the R5CRL server as soon as possible after completion of the run. Raw data to be uploaded include the database file, which requires a library, and the .sif file. Export files, wherein data are extracted and placed in a comma delimited file, may be uploaded at this time.

Please note: Other upload methods may be used, as approved by Metals Group Leader.

10.18.1. If not already logged into the R5CRL server, close all programs and connect as a different user, logging into both the R5CRL server and the XP workstation.

10.18.2. Using Windows Explorer, go to “Volx on ‘R5crl’ (H:),” where x refers to the volume number (Vol1 for CRL). Double click on the Metals folder that appears. Highlight the folder with the appropriate analyst’s name beside it.

10.18.3. Click on File on the command line at the top of the window. Highlight the word New and highlight and click on the word Folder. This will allow the analyst to create a new folder under his or her directory. Create a folder named for the batch number of the samples in the run. Create subfolders for raw data and reports as described in GEN001 (Reference 15.12).

10.18.4. Open Data Manager. Under Tasks, find the function "Create New Library." Choose the subfolder just created for raw data as the destination for the library. The error "No Current Record" will appear, but this only means the library just created contains no data.

10.18.5. With the data file to be copied highlighted, choose Copy from the taskbar, and the new library created above as the destination.

10.18.6. The Export function on the taskbar may be used to copy the data to be used for the reports into the reports subdirectory created above. The data is now in a comma delimited file for further manipulation with a spreadsheet or other data reduction software. This is easiest if the same Design is used repeatedly for the same type of sample.

10.18.7. One Design is used for upload of data to Data Tool. This should be modified only by choosing the analytes and lines to be uploaded and the destination folder.

All fields are chosen, and it creates a comma delimited .prn file and is used with Data Tool as described in section 14.2.4 and 14.2.5.

10.18.8. Use Explorer to copy the .sif file(s) into the raw data subfolder.

11. **QUALITY CONTROL**

11.1. Refer to CRL SOP GEN005 for general quality control information.

11.2. Instrument Check Audits

11.2.1. For every 10-20 samples, instrument checks will be run. One RLC shall be analyzed per instrument run . See Table 2 Appendix A for historical data supporting the limits given below.

Analytical QC Audit ID	Method Limits:*
LCB (TABLE 9.8):	± Method Detection Limits (mg analyte/L)
LCM1, LCM2 & LCMHI (TABLE 9.8):	100 ± 10% Recovery
RLC (TABLE 9.9)	100 ± 50% Recovery

*Any values beyond these limits are flagged.

11.2.2. The solutions analyzed as SIC standards (Section 9.10) are those with which the IEC model has been shown to be imperfect relative to the reporting limit of the analytes that are interfered with. In an ideal model, the contribution from the interfering element would be completely removed, and noise in the signal would be the only component remaining affecting the analyte reading. Some contribution from an interferent may result in a false positive or negative.

11.2.3. SIC results are compared to reporting limits. If SIC results are outside reporting limits, comment is made in the narrative describing the effect of interference on the data. Where the SIC contains more than one element, refer to Appendix ***D for the interelement corrections used for each interferent to gauge the relative contribution from each.

11.2.4. In addition to examining the SIC results, the analyst and reviewer should examine the alternate lines for the analytes on at least one sample. If the result for an analyte is above the reporting limit, and the alternate line has a comparable reporting limit,

the results for the two lines should agree within about 20%. If there is disagreement, the spectra should be examined to see if there is an additional interference that is inadequately corrected. If there is a consistent problem, the IEC table should be reevaluated.

11.2.5. If it becomes apparent through examination of the alternate lines and the **Examine Spectra** window that there is an uncorrected interference on the primary analytical line, and the alternate line gives a better value for the concentration in the sample, the alternate line may be used, if it is of comparable sensitivity. Otherwise, significant changes to the method may be necessary. This should be done in consultation with the Metals Group Leader.

11.3. Digestion Audits:

11.3.1. A complete set of digestion QC are required for every 10 field samples or less with the exception of the digestion blank (LRB) and the digested spike blank (LFB). A LRB and LFB is required to accompany every 20 samples in the batch. Additional blanks and spike blanks may be digested with the sample batch at the analyst's discretion.

11.3.2. Digestion Blank (LRB) - The same volume of Super Q water as used for the samples (typically 50 mL) treated as a sample. All steps used for the samples (*e.g.*, filtration or centrifugation) are also performed on the blank. The digestion blank demonstrates that there is no contamination in the reagents or glassware. The limit for this audit is ± the MDL (Any values beyond these limits are flagged). See also SOP GEN005.

11.3.3. Digestion Matrix Duplicate (LD1) - This is a second aliquot of a field sample treated as a separate sample. Duplicates give an indication of sample homogeneity and consistency of subsampling. The limit for this audit is a relative percent difference (RPD) of ±10% or, near the detection limit, an absolute difference of ± the MDL (Any values beyond these limits are flagged). RPD is defined as:

$$\mathrm{RPD} = \frac{|D - S|}{\left(\frac{D + S}{2}\right)} \times 100 ,$$

where S is the sample result, and
D is the duplicate result.

11.3.4. Digestion Matrix Spike (LSF) - This is a second aliquot of a field sample to which has been added the spiking solutions given in section 9.11. Current practice is to add 1 mL each of the two solutions, A and B, to a 50 mL aliquot. This spiked sample is then processed the same as a regular sample. Low spike recovery on three or more

elements may indicate poor digestion results. For a complex sample low spike recovery may indicate interferences; or, when the duplicate result is taken into account, may indicate a lack of homogeneity or a failure to obtain a representative subsample. A low spike may also be caused by instrument drift. The instrument QC will confirm any instrument drift or nebulizer problem. The limit for this audit is a percent recovery defined as

$$\%\ \mathrm{Recovery} = \frac{(\mathrm{Sp} - \mathrm{S})}{\mathrm{A}} \times 100,$$

where Sp is the result in common units (say mg/L) for the spiked sample,
S is the result for the sample in those same units, and
A is the added spike in those same units.

The limit for this audit is 100 ± 15% (Any values beyond these limits are flagged), up to the point where the sample concentration is twice the added spike. At that point the audit is no longer considered valid. Spiked samples may exceed the linear range for a given channel. These should be diluted and rerun just as any sample would be diluted and rerun for that element. If accuracy audit is invalidated by high source concentration, LFB can be used as accuracy audit.

11.3.5. Digested Spiked Blank (LFB) - This is a blank as in 11.2.1, to which has been added the spiking solutions added in 11.2.3. The equation is the same as for 11.2.3, except the sample is the digestion blank. This equation is

$$\%\ \mathrm{Recovery} = \frac{(\mathrm{LFB} - \mathrm{LRB})}{\mathrm{A}} \times 100,$$

where LFB is the concentration measured of the LFB,
LRB is the concentration measured of the LRB, and
A is the amount of added spike.

The limit for this audit is 100 ± 15% (Any values beyond these limits are flagged).

11.3.6. The frequency of digestion QC is as described in section 11.2.1. If the field sampler has designated a sample for matrix QC, that is the sample to be used. Additional samples may be chosen at the analyst's discretion, save for designated field blanks. A field blank may not be used for the duplicate or spiked sample.

11.4. Acceptance of Run/Element Data:

11.4.1. When analyzing simultaneously for many elements, it is statistically predictable that some audits will be outside the stated limits due to random error. However, there is no generally accepted statistical method for determining that an analysis is in control when an audit has exceeded control limits. If an element of interest to the requestor is out of control for an audit, the samples shall be re-analyzed, or re-prepared and re-analyzed, as needed. These steps may be avoided if, after discussion with the requestor, the failed audit is found to have little effect on the intended use of the data. Data Quality Objectives (DQOs) should be part of a quality assurance project plan (QAPP) received with the samples. These should give action limits and intended use of the data.

11.4.1.1. If these are not present, discussion with the sampler or the project manager can help with the decision whether reanalyses is necessary. For example, if an element is found in the blank above the detection limit, or the spike recovery for the element is high, but all results for the element are below the action level for the Program, the data are useable.

11.4.2. The run must be reviewed for systematic errors. Systematic errors may be found in at least three categories: Contamination, which may be random or consistent; drift of baseline; or drift of slope. This by no means covers all types of error, rather only the most common. Evidence of systematic error would be cause for rejection of an element from a run or, in extreme cases, rejection of the run.

11.4.2.1. Systematic errors from low level contamination are difficult to spot, but can be diagnosed by examination of blanks and field blanks. Duplicates and spikes may also show low level contamination if the concentration in the sample itself is low. Field blanks should be confirmed to show that the contamination does not arise from the laboratory. One member of a duplicate or spike pair may be elevated by contamination, throwing the audit out of control. The pattern of all the audits from a digestion run must be examined for evidence of contamination. The Group Leader or QC Coordinator may choose to have the run redigested for that element.

11.4.2.2. Systematic errors from baseline drift, if positive, may appear to be similar to the contamination mentioned above. It is easily confirmed while running by aspirating the calibration blank. It is less easily diagnosed after the run is over. Negative drift is equally to be avoided because false negatives can result.

11.4.2.2.1. It is quite possible that the other audits, LCM's, duplicates and spikes, may be in control even if the blanks show unacceptable drift.

11.4.2.3. Drift of slope rarely affects only one channel. The nebulizer may clog, or the plasma may get hotter or cooler in the course of the run. These problems

will affect different elements differently, and may cause drift in different directions. The instrument QC should be examined not only to show if they are in or out of control, but for trends. For example, a low LCM, within control but biased low, may indicate why a spike for that element becomes flagged. Drift may affect only a portion of a run, in which case only that portion needs to be rerun.

11.4.3. Corrective action when the quality control is outside limits depends on the severity of the violation and on the statistical nature of multianalyte analysis.

11.4.3.1. If the violation affects the determination of a violation of program limits or the DQOs of the project, the first recourse is for reanalysis. If repreparation is necessary, the presence of sufficient sample to carry this out is a factor. Similarly, holding time is a factor. If reanalysis is not possible, this must be explained to the client.

11.4.3.2. If the violation is not critical, the corrective action hinges on the statistics. Typically, 5% of the determinations may exceed the limits. If the number of violations exceeds this amount, an examination must be made as to whether the samples were overly difficult or the instrument requires maintenance. If the former, repreparation may be needed to verify this. If the latter, the digests may need to be reanalyzed after the maintenance is performed.

11.4.4. Any quality control limit violations shall be flagged on the data as described in section 4 of CRL SOP GEN005.

11.5. The measurement of the method detection limit is performed by the procedure specified in CRL QMP Appendix 1. The reporting limit is determined to be 3 to 5 times this value, and this becomes the concentration of the RLC solution mentioned in section 9.9. How often the MDL must be determined is a function of instrument conditions and historical quality control data. CRL policy is now for MDLs to be renewed annually.

11.5.1. If the instrument has had major work done to the spectrometer, then a measurement of a new MDL must be performed.

11.5.2. If there is a change to the SOP or the instrument method, such as changing forward power, changing wavelengths, correction scheme, mode of viewing, or a change in the calibration range.

11.5.3. If there is a trend observed in the historical data obtained on the digestion blank (LRB) or on the recovery of the RLC, as displayed in the control charts or range charts (Reference 15.14), then a measurement of a new MDL must be performed. If there is a question about what constitutes a significant trend, consult the Metals Group Leader.

11.5.4. If it is clear from the range chart wherein the absolute value of either the LRB or LCB is plotted that the statistical MDL determined above is too small to be practical, the 3 standard deviation value from the range chart is used to evaluate the LCB and LRB on a routine basis. This result will be termed the practical MDL.

12. **PREVENTATIVE MAINTENANCE**

12.1. Inspect the pump tubing before operating. Tubing can be stretched gently 10 times by hand before installation. An awl is inserted into the tubing before installation to stretch it. When pump is not in use, release the pressure plate and release the tubing to prevent flat spots from forming.

12.2. The following should be regularly checked:

12.2.1. Air filters: clean or replace as necessary, typically twice per year.

12.2.2. Pneumatic filters: check the argon dryer filter, and argon filters for moisture.

12.2.3. The torch, glassware, and aerosol injector tube. The glassware should be clean, with no trace of deposits or signs of melting. Devitrification will occur, but over time in severe cases, cracking will take place. If the torch cracks, the shape of the plasma will change, and the operating characteristics will deteriorate. The torch should be replaced if cracking occurs.

12.2.4. The nebulizer for clogs and the sample capillary tubing for build -up and tube wear. The nebulizer can be removed and placed in a sonicator bath with the wash solution (section 9.4) to clean it.

12.2.5. The radial window is subject to collect sample material if very high solids samples are run. The need to clean the window can be monitored by examination of the standard absolute intensities for selected elements. Follow the procedure in the hardware manual for removal and replacement. Generally, the deposits can be removed with sonication in a nitric acid solution.

12.2.6. If the argon supply is allowed to deplete, the spectrometer will go to standby mode. It is best to turn the spectrometer power off if this occurs. After the argon supply is restored, the instrument will require a warmup, which is conducted in the Diagnostics window. Allow 73 min. for the warmup, and may need to be done twice. It has been observed that even after this warmup, the instrument still requires a day of having argon to become stable.

> Please Note**:** Perform the warmup as soon as possible after connecting the new argon supply. There are certain hardware functions that do not perform until this software operation is performed.

12.3. If maintenance has been done on the torch compartment, an alignment of the spectrometer viewing optics should be performed. This is done from the Tools option of the menu bar, under Spectrometer Control. For radial view, a 10 mg/L Mn solution is aspirated and the torch viewing position is optimized. For axial view, a 1 mg Mn/L solution is used. This optimization can also be performed as a normal maintenance routine.

12.4. All maintenance must be recorded in the instrument logbook. This includes simple daily functions such as replacing pump tubing.

13. **TROUBLESHOOTING**

13.1. Interferences are discussed in Section 5.

13.2. Equipment problems are discussed in Section 12.

13.3. Analytical performance cautions are given in Section 4.

13.4. Corrective actions when QC is outside are given in Section 11.

13.5. If the plasma does not initiate, consider replacing o-rings. Any air leak into the argon flow will prevent the plasma from forming.

13.6. Monitor the intensities of the internal standard. This will be affected by the condition of the radial and axial windows and the performance of the nebulizer. During the run, a lowered intensity of the internal standard may be a sample matrix effect. The RSD of the internal standard should be near 1% or lower. This will be affected by the pump tubing, the nebulizer, and any flickering of the plasma. A high solid sample will also raise the RSD and lower the internal standard intensity. A very high count can indicate the probe did not withdraw sample. A consistently high RSD will indicate that the either the sample delivery or the plasma torch or generator requires maintenance.

13.7. If an analytical line of importance shows behavior such as strong negative concentrations for blanks and other low samples, open the **Examine Spectrum** window and select the current run. Select all the samples, and select the affected element's lines. Under **Graph**, select **Define Y-axis** and manually select an appropriate number of counts under the manual settings to view the calibration blank. If a peak is present in the blank, and is there for the other lines of comparable sensitivity, the calibration blank was contaminated or the sample introduction lines were dirty. The system should be pumped with 20% HCl and the calibration restarted.

13.8. Any time an element of importance shows odd behavior, either strongly negative, or there is serious (>20% RPD) difference between lines of comparable sensitivity and the result is more than five times reporting limit, the **Examine Spectrum** window should be

examined to see if there is a previously undocumented spectral interference, or the background correction point is misplaced. If background correction points are moved, the IEC tables should be redetermined. IEC spectra are maintained on R5CRL, so they are available for reprocessing, if necessary. Anytime such a serious change is made, the method must be given a new name.

13.9. Also in **Examine Spectrum** window, peak position can be checked and readjusted per instruction from Perkin Elmer.

13.10. The plasma will not initiate if the spray chamber is flooded. This can occur if the drain tubing was misaligned or improperly plumbed, so verify that bubbles are exiting through the clear tubing on the spray chamber drain side soon after the sample pump starts. If the spray chamber is flooded, recheck tube plumbing and also the tube clamps at the peristaltic pump. Set the pump On for several minutes to empty the spray chamber. If an attempt to initiate the plasma fails, examine the torch for signs of water. If there is water on the torch, turn on Plasma and Aux flows. Raise the Aux flow to 1.5 L/min from 0.5 L/min for about 30 minutes, but be sure to lower the flow back to 0.5 L/min before starting a method. If this does not dry out the water from the torch and the plasma does not initiate, then the torch assembly will need to be removed, dried, and remounted.

14. **LIMS ENTRY AND REPORTING**

14.1. All LIMS data entry is based on first creating a bench sheet describing the sample preparation. This bench sheet describes the samples prepared, and the digestion quality control samples. The stock spike solutions described in section 9.11 are used here for the matrix spike and blank spike. The analyst must make certain that the preparation date in LIMS matches the actual preparation date. By convention, if the sample preparation proceeds overnight, the date started is used for the LIMS preparation date. Only one blank and blank spike are needed per digestion batch.

14.2. When the data are ready to be entered, the bench sheet is called up into the Data Entry/Review module. All analyses or selected analyses can be included. If only a few analyses are to be entered, data may be entered manually. Otherwise, it may be more practical to use Data Tool.

14.2.1. When performing manual data entry, enter the results in the column **Result** in mg/L. For each result, enter the date of analysis in the column **Analyzed**. This column has a calendar feature as do other date fields in LIMS. If dilutions were necessary for the analysis, enter the dilution in the column **Dilution**. The sample result should be the one measured and not corrected for the dilution factor. Verify that the correct initials are present in the Analyst field and the instrument field.

14.2.2. If all data are entered, click the **Save** button on the top row. After saving, proceed to the Review page by clicking **Query** on the second row. Verify that all

conversions to reporting units and dilutions have been calculated correctly. Verify that reporting limits have been correctly applied. Flags may be added at this stage, following the guidance given in SOP GEN005. Before review by the peer, The data may be locked, and the status should be updated to Analyzed.

14.2.3. If Data Tool is to be used, once the batch is called up in Data Entry/Review, click **Export** to create an Excel file in the User Directory. Name this file in a manner that it can be easily associated with that analysis. If totals and dissolved pairs are analyzed in the same batch, create a separate Excel Export file for each of the two analyses.

14.2.4. A file created in section 10.15.7 (a .prn file) contains the instrument readings for the samples. If multiple measurements for a given sample are present, such as for dilutions, the .prn file can be loaded into a text editor, such as Word Pad, and the sample IDs for the sample readings that are not to be used can be altered so that Data Tool does not recognize them. This altered file must be saved as a .prn file for Data Tool to use it. Optionally, Data Tool allows for changing the names identified at the instrument. In the DataTool's main screen, click Merge Files. To rename samples, select the Instrument Data tab and right click Lab_Number and click Replace. Before saving the merged file, click on Refresh.

14.2.5. Once in Data Tool, click **Browse** for the Element Data Entry Table, and call up the .xls file created in 14.2.3. Click **Browse** for the Instrument Data File, and call up the file created in 10.15.7. If unneeded sample entries remain in the lower left-hand box, click **Clear**. Double-click on the desired .prn file and either **Auto Select** or highlight individual samples and click **Include**.

Additionally, Data Tools already allows for changing the names identified at the instrument. In the DataTool – Main screen, click Merge Files. To rename samples, select the Instrument Data tab and right click Lab_Number and click Replace. Before saving the merged file, click on Refresh.

14.2.6. Once the samples and digestion quality control are selected, click **Done** and it will return to the main Data Tool page. Click **Merge Files**. If either Unmatched Analytes or Unmatched Units appear in red, repair the cross table with the assistance, if necessary, of the Metals Group Leader. Verify that the results in Initial Result are correct, and click **Save**, which will create an Excel file. Name this one differently from the name chosen in 14.2.5 and click **Done**.

14.2.7. Return to the Data Entry/Review module and click **Open**, using the .xls file created in the paragraph above. Verify that all items are correct as in the manual data entry in 14.2.1 and click **Save**. Query the data and proceed as in 14.2.2.

14.2.8. Note that only one analytical line is used per element for Data Tools. In Data Tool, the Analyte Cross Table can be set with upper concentration limits for each

analytical wavelength. For analytes with high and low channels, such as aluminum, iron and manganese, this information allows Data Tool to select the correct wavelength. This is done by correcting the Data Range entry. For iron, Data Tool can be made to select the Fe 259.939 nm line for digest concentrations up to 10 mg/L and Fe 273.955 nm for concentrations up to 500 mg/L. Note if there is a concentration of over 500 mg/L in this case, Data Tool will import nothing.

14.3. LIMS Report Generation

14.3.1. Once all ICP data are entered with the status of Analyzed, prepare a draft report. In LIMS, select Project Management, Reports. Choose the work order and the analyses, and select the report. C_Sample_Metals and C_Sample_Metals_NoQC print out samples one per page. This format is best to choose when reporting the full suite of analytes. C_Analysis_Metals and C_Analysis_Metals_NoQC print out results with multiple samples per page. This format is best used when a limited suite of analytes is being reported, and saves paper. If QC is to be omitted from the report, such as with a prep batch shared with ICP, including separate spikes for the two methods, choose Modified Draft, unchecking the quality control samples that were not analyzed. This draft report need not be signed. It is only for the purpose of review.

14.3.2. After the peer reviewer has updated the status of the LIMS entries to Reviewed, the final report may be generated. The mode of generation of the report is the same as above, except that C_Sample_Metals_NoQC.rpt or CE_Sample_Metals_NoQC.rpt would be chosen, and either the Final Report or Modified Final Report is chosen. Again, if only a few analytes are reported, C_Analysis_Metals.rpt can be used. All pages of the report and the transmittal form must be signed and dated.

14.4. For any batch there is a standard set of documents which accompany the data to the evidence files. See the Data Package Requirements Section of the Standard Operating Procedure for the Review of Data Produced in the Analysis for Metals in Environmental Samples, GEN005. The standard set includes:

14.4.1. The original and a copy of the values reported from LIMS for the samples of the batch, including the transmittal form.

14.4.2. An original and a copy of the narrative which describes the analysis and assists the client in evaluating the quality of the data. The requirements for the narrative are described in SOP GEN005.

14.4.3. A copy of the digestion sheet which indicates what samples were digested, who performed the digestion, the date the digestion was performed, the method by which the samples were digested and which shows what other batches, if any, were in the same digestion group.

14.4.4. A copy of the results for all the digestion QC (blanks, duplicates and spikes) of the digestion group. Occasionally, part of a run will be reported because something went wrong with digestion QC in one of the sample groups (ten samples and attendant QC). In this case only the acceptable QC is included in the file. The decision to report only part of a run requires consideration of many factors in the entire run and must be made with consultation among the analyst, group leader and/or the QC coordinator.

14.4.5. A copy of the instrument quality control checks report, including LCB, LCM1, LCM2 and LCMHI. Also include a report of the RLC and SIC solutions. Rarely, part of a run will be reported because something went wrong with instrument QC after one of the sample groups (ten samples and digestion QC). In this case only the acceptable QC is included in the file. The decision to report only part of a run requires consideration of many factors in the entire run and must be made with consultation among the analyst, group leader, and/or the QC coordinator.

14.5. The information listed in 14.4 is submitted to a peer reviewer and other reviewers in a standard order to aid in the data review. The sample values are paper clipped to a QC package that is clipped together and is the same for all samples in the digestion group. The QC package is in the order of digestion preparation sheet, LCB, LCM1, LCM2, LCMHI, RLC, LRB, LFB, duplicate, spike, SICs, and other supporting information (*e.g.*, undigested field blank analysis). Any comments or notes about the QC package or samples is written in a separate narrative, that must be submitted with the data package.

14.5.1. The QC package shall use the analysis summary page described in section 6.3.2 of CRL SOP GEN005 as a cover page. The internal standards shall be summarized on this page. Spreadsheet software may be used to generate this and subsequent pages.

14.5.2. The LCB shall be evaluated against the MDL for each analytical line used, with a flag for any line exceeding either plus or minus the limit.

14.5.3. The LCM1, LCM2 and LCMHI shall be evaluated as a percent recovery, with the limits given in section 11.1.1 as acceptance limits.

14.5.4. The RLC is evaluated as a percent recovery, with the limits given in section 11.1.1 as acceptance limits

14.5.5. The LRB shall be evaluated against the MDL for each analytical line used, with a flag for any line exceeding either plus or minus the limit.

14.5.6. The LFB shall be evaluated as given in section 11.2.4, calculating percent recovery.

14.5.7. The duplicate shall be evaluated calculating both absolute difference, evaluated against the MDL, and RPD, evaluated as given in section 11.2.2. If either of these limits is met, the duplicate is valid.

14.5.8. The matrix spike shall be evaluated as a percent recovery, as given in section 11.2.3. If the sample is more than twice the added spike the spike cannot be used to evaluate the element for an accuracy audit.

14.5.9. The SIC solutions are evaluated against the reporting limit. Any lines exceeding this limit will be flagged.

14.6. The original raw data is submitted with the completed data packages, after peer review, to the group leader for final submission. After the final CRL review the raw data is placed with the appropriate sample batch by the data coordinator. The first sheet of the raw data should be initialed and dated by the analyst. Any unusual occurrences during the run should be noted, initialed and dated on the raw data.

14.7. The instrument raw data file(s) and all other electronic files related to the sample batch is uploaded to R5CRL. See Protocol for Upload of Inorganic Data to R5CRL, Revision 7 (SOP GEN001).

14.8. The client normally receives a signed and dated copy of the report generated in section 14.3.2 plus the narrative. If the QAPP has called for independent data validation of the data package, copies of the raw data, bench sheet, run log, quality control summary report, and any other bench notes are copied for the client. Items not to be included are the checklist, the memo giving paths to the data storage on R5CRL, the work order listing, and the copy of the narrative initialed by the deputy director.

15. **REFERENCES**

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15.4. "An Atlas of Spectral Interference in ICP Spectroscopy", M. L. Parsons, A. Foster, and D. Anderson (Plenum, New York) 1980.

15.5. Massachusetts Institute of Technology Wavelength Tables G. R. Harrison, ed. (M.I.T. Press, Cambridge, Massachusetts) 1969.

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15.8. Standard Operating Procedure for the Digestion of Aqueous and Solid Samples by Method 200.2, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. METALS025.

15.9. Standard Operating Procedure for the Digestion of Aqueous and Solid Samples for Metals Hotplate Digestion, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. METALS033.

15.10. Standard Operating Procedure for the Review of Data Produced in the Analysis of Metals in Environmental Samples, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. GEN005.

15.11. Standard Operating Procedure for the Digestion of Aqueous Samples Using Microwave Heating, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. METALS035.

15.12. Protocol for Upload of Inorganic Data to R5CRL, Revision 5, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML-10C) Chicago, Illinois 60605. GEN001.

15.13. Quality Management Plan, U.S. Environmental Protection Agency, Region 5 Central Regional Laboratory, 536 South Clark Street (ML- 10C) Chicago, Illinois 60605.

15.14. J. K. Taylor, *Quality Assurance of Chemical Measurements*, Lewis Publishers, Inc., Chelsea, Michigan, 1987, Chapter 14.

Appendices

Appendix A –

Table I. Method Detection Limits

The method detection limits (μg/L), reporting levels (μg/L), limits of linearity (μg/L) and the plasma view for the two instrumentsare listed below (not all lines are included; only the primary lines for reporting are given):

Element/ Wavelength	Method Detection Limit (μg/L)	Reporting Level (μg/L)	Linearity Limit (μg/L)	Plasma View
Ag 328.068**	1.1	5	100	Axial
Ag 338.289	2.0	8	100	Axial
Al 308.215 **HI**	28	100	5,000,000	Radial
Al 396.153	30	100	2,250,000	Radial
As 188.979**	6	20	500,000	Axial
As 193.696	3.3	20	250,000	Axial
B 249.677	19	50	250,000	Radial
Ba 455.403	0.9	3	25,000	Radial
Be 313.042	0.3	1	25,000	Axial
Ca 315.887	58	200	1,000,000	Radial
Cd 214.440**	0.4	2	7,500	Axial
Cd 226.502	0.3	2	25,000	Axial
Co 228.616	0.9	3	25,000	Axial
Cr 267.716	1.5	5	10,000	Axial
Cu 324.752**	1.4	5	50,000	Axial
Cu 327.393	0.9	5	100,000	Axial
Fe 259.939	16	50	1,000,000	Radial

Element/ Wavelength	Method Detection Limit (μg/L)	Reporting Level (μg/L)	Linearity Limit (μg/L)	Plasma View
Fe 273.955 **HI**	16		5,000,000	Radial
K 766.490	150	800	5,000,000	Radial
Li 670.784	7.7	25	250,000	Radial
Mg 279.077 **HI**	22	100	10,000,000	Radial
Mg 280.271	6	500	100,000	Radial
Mn 257.610	0.4	1	100,000	Radial
Mo 202.031**	1.2	4	100,000	Axial
Mo 204.597	1	4	100,000	Axial
Na 589.592	120	400	1,000,000	Radial
Ni 231.604	1.4	3	25,000	Axial
Pb 220.353	3.4	15	100,000	Axial
Sb 206.836	6.1	20	500,000	Axial
Se 196.026	8.8	20	100,000	Axial
Sn 189.927	2.4	10	100,000	Axial
Sr 407.771	0.3	2	10,000	Radial
Sr 421.552	0.5	2	50,000	Radial
Ti 334.940**	1	5	100,000	Radial
Ti 336.121	2	5	100,000	Radial
Tl 190.801	5	20	25,000	Axial
V 292.402	1.5	5	100,000	Axial
Zn 213.857	4.8	30	50,000	Radial

** Default line
HI High channel

The date of verification of MDLs was January 2008

The date of verification of linearities was December 2006

Table II. Historical Data Results

The calibration verification mean and true value (μg/L) and ± 3 s (%), and the RLC mean and true value (μg/L) and ± 3 s (%) for the 4300 DV are listed below (not all lines are included; only the primary lines for reporting are given):

Element/ Wavelength	CV mean (true) (mg/L)	± 3 s %	RLC mean (true) (mg/L)	± 3 s %
Ag 328.068	0.461 (0.5)	10.6	0.0047 (0.005)	56.9
Al 308.215 **HI**	99.5 (100)	20.5	0.0997 (0.1)	47.4
Al 396.(1)53	0.962 (1)	11.2	0.106 (0.1)	36.9
As 188.979	2 (2)	7.09	0.0209 (0.02)	36.9
B 249.677	0.994 (1)	8.27	0.0477 (0.05)	30.4
Ba 455.403	0.997 (1)	9.14	0.0029 (0.003)	21.8
Be 313.042	0.998 (1)	8.87	0.001 (0.001)	21.8
Ca 315.887	101 (100)	13.4	0.231 (0.2)	30.9
Cd 214.440	1 (1)	10.2	0.0014 (0.002)	538
Co 228.616	0.994 (1)	9.47	0.0029 (0.003)	27.6
Cr 267.716	0.993 (1)	8.63	0.0051 (0.005)	20.9
Cu 324.752	1 (1)	9.99	0.0054 (0.005)	61.6
Fe 259.939	1.04 (1)	8.54	0.051 (0.05)	35.1
Fe 273.955 **HI**	107 (100)	20.8	0.0557 (0.05)	44.4
K 766.490	95.3 (100)	10.1	0.805 (0.8)	30.7
Li 670.784	1 (1)	10.1	0.0251 (0.025)	25.1

Element/ Wavelength	CV mean (true) (mg/L)	± 3 s %	RLC mean (true) (mg/L)	± 3 s %
Mg 279.077 [HI]	60.1 (60)	21.3	0.101 (0.1)	61
Mg 280.271	1 (1)	13.1	0.0947 (0.1)	59.8
Mn 257.610	0.994 (1)	10.8	0.001 (0.001)	65.7
Mo 202.031	0.961 (1)	7.35	0.0041 (0.004)	18.8
Na 589.592	95.3 (100)	8.77	0.45 (0.4)	34.3
Ni 231.604	1.02 (1)	9.18	0.0032 (0.003)	41.8
Pb 220.353	1.92 (2)	12.5	0.0123 (0.015)	317
Sb 206.836	1.97 (2)	7.76	0.0203 (0.02)	26.8
Se 196.026	1 (1)	10.3	0.0324 (0.03)	31
Sn 189.927	4.79 (5)	5.01	0.0103 (0.01)	30.6
Sr 421.552	1 (1)	8.76	0.0019 (0.002)	24.5
Ti 334.940	1 (1)	9.91	0.005 (0.005)	11.4
Tl 190.801	4.98 (5)	12.8	0.0186 (0.02)	71.9
V 292.402	0.981 (1)	8.8	0.0049 (0.005)	17.4
Zn 213.857	0.977 (1)	13.5	0.0296 (0.03)	35.6

[HI] High channel

Appendix B

Uncertainty Calculation

Uncertainty in the method for determination of metals in waters and wastewaters by ICP-OES is estimated by statistical evaluation of the spiked blank results. The standard deviations are calculated on the basis of percent recovery of the spike. The statistical method described in CRL SOP GEN006 is used. Because the number of elements reported for a set of samples may vary, the number of data points per element is different in the table below.

Uncertainty by Element				
Element	Spike Conc. (mg/L)	Standard Dev. (% rec)	Number of Points	Uncertainty (%)
Aluminum	1.0	5.19	25	2.19
Antimony	0.5	5.67	24	2.45
Arsenic	0.2	11.8	25	4.97
Barium	0.2	3.87	25	1.63
Beryllium	0.01	9.31	24	4.02
Boron	1.0	7.81	22	3.54
Cadmium	0.05	4.17	25	1.76
Calcium	50.0	4.69	25	1.98
Chromium	0.1	4.88	25	2.06
Cobalt	0.1	4.24	24	1.83
Copper	0.1	4.66	24	2.01
Iron	1.0	4.8	25	2.02
Lead	0.5	5.02	25	2.11
Lithium	0.1	4.92	20	2.36
Magnesium	20.0	4.98	25	2.10
Manganese	0.2	4.6	24	1.98
Molybdenum	0.1	4.36	24	1.88

Uncertainty by Element				
Element	Spike Conc. (mg/L)	Standard Dev. (% rec)	Number of Points	Uncertainty (%)
Nickel	0.2	3.94	24	1.70
Potassium	0.25	3.62	24	1.56
Selenium	0.5	5.42	25	2.28
Silver	0.025	5.02	25	2.11
Sodium	50.0	4.7	25	1.98
Strontium	1.0	4.59	24	1.98
Thallium	0.5	6.25	23	2.76
Tin	0.5	3.57	24	1.54
Titanium	0.1	4.34	24	1.87
Vanadium	0.1	4.75	24	2.05
Zinc	1.0	4.49	25	1.89

As stated in section 1.5 of this SOP, this uncertainty will be greater near the reporting limit and will be much greater near the MDL. Usually, the sampling component of the uncertainty will be far greater than the laboratory uncertainty.

Appendix C
Differences Between SOP Metals 003 and EPA Method 200.7

1. Mercury, phosphorous and silica are not currently part of this SOP.

2. The matrix for the standards is 1% HNO_3 and 0.5% HCl, to match the samples, which are prepared by methods 200.2 without the 2-fold concentration step. This limits the silver concentration to 0.1 mg/L.

3. Interelement correction factors are used as the WinLab 32 software generates them. They are not evaluated by the procedure given in 7.13 of 200.7.

4. The torch plasma viewing positions are evaluated using the WinLab 32 software using 1 mg Mn/L, as recommended by the manufacturer.

5. All quality control checks are done using solutions from a different source from the calibration standards. Thus, the IPC and QCS are not different in this method.

6. LCMs are evaluated to ±10% throughout the procedure, rather than ±5% at the beginning of the run. This is to avoid problems with the instrument software.

Appendix D
SIC Tables

SIC Co V						
	Co	V			Co	V
Ag 328.068	0	-0.128985		Mg 279.077	-1.11129	0
Ag 338.289	0	0		Mg 280.271	0	0.336894
Al 308.215	0	13.0014		Mg 285.213	0	-0.129423
Al 394.401	0	0.14383		Mn 257.610	0	-0.00860235
Al 396.153	0	0		Mn 259.372	0	0
As 188.979	0	0		Mn 260.568	0.656859	0.0174999
As 193.696	0	0.241116		Mo 202.031	0	0
As 197.197	0	0		Mo 203.845	0	0
B 208.889	0	0		Mo 204.597	0	0
B 249.677	1.13829	0		Na 588.995	0	0
B 249.772	-0.749239	0		Ni 221.648	-0.0353675	0.0359515
Ba 233.527	0	0.434273		Ni 231.604	0.331823	0
Ba 455.403	0	-0.0128153		Ni 232.003	-0.102043	0.0343799
Ba 493.408	0	0		P 213.617	-4.71776	0
Be 234.861	0	0		P 214.914	0	-0.789356
Be 313.042	0	1.27444		Pb 217.000	0	0.430311
Be 313.107	0	0		Pb 220.353	0	0
Ca 315.887	1.51197	0		Sb 206.836	0	-0.223334
Ca 317.933	0	0		Sb 217.582	0.189201	1.81351
Cd 214.440	0	0		Se 196.026	-0.122319	0
Cd 226.502	-0.00468924	0		Se 203.985	0.459431	**0**
Cd 228.802	0.184712	0.045207		Si 251.611	0	0
Ce 413.380	0	0.447952		Si 252.851	103.908	767.39
Ce 413.764	0	0		Si 288.158	0	**0**
Ce 418.660	0	0		Sn 189.927	0	0
Co 228.616	0	0		Sn 235.485	-2.35073	0
Co 230.786	0	0		Sr 407.771	0	0
Co 238.892	**n/a**	0.231433		Sr 421.552	0	0
Cr 205.560	0	0		Sr 460.733	0	0
Cr 267.716	0	0.0303129		Ti 334.940	0	0
Cr 283.563	0	0.0374634		Ti 336.121	0.0273743	0
Cu 224.700	0	0		Ti 337.279	-0.101414	0
Cu 324.752	-0.0155505	-0.136724		Tl 190.801	4.13699	2.27154
Cu 327.393	0.223696	0		Tl 276.787	0	**-16.4276**
Fe 238.204	0.0481692	0.0218802		Tl 351.924	0	2.3709
Fe 239.562	0.503374	0		V 292.402	0	0
Fe 259.939	0	0		V 310.230	0	**n/a**
Fe 273.955	0	1.74246		V 311.071	0	0
Li 610.362	0	0		Zn 202.548	0	0
Li 670.784	0	0		Zn 206.200	0	0
				Zn 213.857	0	**-0.0541124**
021507.iec						

SIC Cr Mo						
	Cr	Mo			Cr	Mo
Ag 328.068	0	0.0350511		Mg 279.077	-1.11129	0
Ag 338.289	1.52885	0.014466		Mg 280.271	0	0.336894
Al 308.215	0	12.4034		Mg 285.213	0	-0.129423
Al 394.401	0	2.39829		Mn 257.610	0	-0.00860235
Al 396.153	0	37.4189		Mn 259.372	0	0
As 188.979	0.643513	0		Mn 260.568	0.656859	0.0174999
As 193.696	0.865551	0.491911		Mo 202.031	0	0
As 197.197	0	0		Mo 203.845	0	0
B 208.889	0.0693604	0		Mo 204.597	0	0
B 249.677	0	0		Na 588.995	0	0
B 249.772	0.0500508	0		Ni 221.648	-0.0353675	0.0359515
Ba 233.527	0	-0.796894		Ni 231.604	0.331823	0
Ba 455.403	0	0		Ni 232.003	-0.102043	0.0343799
Ba 493.408	0	0		P 213.617	-4.71776	0
Be 234.861	0	-0.0856369		P 214.914	0	-0.789356
Be 313.042	-0.0230347	0		Pb 217.000	0	0.430311
Be 313.107	-0.063265	0		Pb 220.353	0	0
Ca 315.887	0.707829	2.44302		Sb 206.836	0	-0.223334
Ca 317.933	0.66531	0.922494		Sb 217.582	0.189201	1.81351
Cd 214.440	0	0		Se 196.026	-0.122319	0
Cd 226.502	0	0		Se 203.985	0.459431	**0**
Cd 228.802	0	0		Si 251.611	0	0
Ce 413.380	0.0157518	0		Si 252.851	103.908	767.39
Ce 413.764	0	0.110532		Si 288.158	0	**0**
Ce 418.660	0.284653	-10.3945		Sn 189.927	0	0
Co 228.616	0.0422941	0		Sn 235.485	-2.35073	0
Co 230.786	0.0857869	0.406815		Sr 407.771	0	0
Co 238.892	0	-0.412672		Sr 421.552	0	0
Cr 205.560	**n/a**	0.413053		Sr 460.733	0	0
Cr 267.716	0	0.0872483		Ti 334.940	0	0
Cr 283.563	0	-0.0251702		Ti 336.121	0.0273743	0
Cu 224.700	0	1.40795		Ti 337.279	-0.101414	0
Cu 324.752	0	0.281762		Tl 190.801	4.13699	2.27154
Cu 327.393	0	-0.145238		Tl 276.787	0	**-16.4276**
Fe 238.204	0.0404021	0		Tl 351.924	0	2.3709
Fe 239.562	0.0859441	0.131181		V 292.402	0	0
Fe 259.939	0	0		V 310.230	0	**n/a**
Fe 273.955	.1.03931	0		V 311.071	0	0
Li 610.362	0	0		Zn 202.548	0	0
Li 670.784	0	0		Zn 206.200	0	0
				Zn 213.857	0	**-0.0541124**
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SIC Cu Ti						
	Cu	Ti			Cu	Ti
Ag 328.068	0	0		Mg 279.077	0	0
Ag 338.289	0	-11.3201		Mg 280.271	0	0
Al 308.215	0	0		Mg 285.213	0	0
Al 394.401	0	0		Mn 257.610	0	0
Al 396.153	0	0		Mn 259.372	0	0
As 188.979	0	-3.14776		Mn 260.568	0	0
As 193.696	0	0		Mo 202.031	0	0
As 197.197	0	0		Mo 203.845	0	0
B 208.889	0	0		Mo 204.597	0	0
B 249.677	0	0		Na 588.995	0	0
B 249.772	0	0		Ni 221.648	0	0
Ba 233.527	0	0		Ni 231.604	0	0
Ba 455.403	0	0		Ni 232.003	-0.245797	-0.0939162
Ba 493.408	0	0		P 213.617	60.3149	0
Be 234.861	0	0		P 214.914	6.38355	0
Be 313.042	0	0		Pb 217.000	-3.04239	0
Be 313.107	0	0.127048		Pb 220.353	0	0
Ca 315.887	0	0		Sb 206.836	0	0
Ca 317.933	0	0		Sb 217.582	0	-0.244908
Cd 214.440	0	0		Se 196.026	0	0
Cd 226.502	0	0.0249318		Se 203.985	0	0
Cd 228.802	0.0173254	0		Si 251.611	0	0
Ce 413.380	0	0		Si 252.851	0	0
Ce 413.764	0	0		Si 288.158	0	0
Ce 418.660	0	0		Sn 189.927	0	-0.314443
Co 228.616	0	2.0428		Sn 235.485	0	-1.51979
Co 230.786	0	0		Sr 407.771	0	0
Co 238.892	0	0		Sr 421.552	0	0
Cr 205.560	0	0		Sr 460.733	0	0
Cr 267.716	0	0		Ti 334.940	0.0341905	0
Cr 283.563	0	0		Ti 336.121	0	0
Cu 224.700	n/a	0		Ti 337.279	0	n/a
Cu 324.752	0	0.189225		Tl 190.801	0	0
Cu 327.393	0	0.321183		Tl 276.787	0	0.158097
Fe 238.204	0	0		Tl 351.924	0	1.89177
Fe 239.562	0	0		V 292.402	0	0.567612
Fe 259.939	0	0		V 310.230	0	0
Fe 273.955	0	0		V 311.071	0	11.6819
Li 610.362	0	0		Zn 202.548	7.07095	0
Li 670.784	0	0		Zn 206.200	0	0
				Zn 213.857	0.857657	0
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SIC Fe Mn						
	Fe	Mn			Fe	Mn
Ag 328.068	-0.00522769	0		Mg 279.077	0.39505	0
Ag 338.289	0.0008143	0		Mg 280.271	0	0
Al 308.215	0	0.400182		Mg 285.213	0.00991829	0
Al 394.401	0.0351911	0		Mn 257.610	0.0109139	0
Al 396.153	0	0		Mn 259.372	1.11353	0
As 188.979	0	0		Mn 260.568	0.0420497	**n/a**
As 193.696	-0.724821	0		Mo 202.031	-0.031366	0
As 197.197	0	0		Mo 203.845	0	0
B 208.889	0.042494	0		Mo 204.597	0	0
B 249.677	-0.0601562	0		Na 588.995	0	0
B 249.772	1.15451	0		Ni 221.648	0	0
Ba 233.527	0.0225804	0		Ni 231.604	0	0
Ba 455.403	0	0		Ni 232.003	-0.547792	0.158188
Ba 493.408	0.00236943	0		P 213.617	-1.0958	0
Be 234.861	0.0922713	0		P 214.914	0.894392	0
Be 313.042	0	0		Pb 217.000	0.368193	0
Be 313.107	0	0		Pb 220.353	0.0579035	0
Ca 315.887	0	0		Sb 206.836	0	0
Ca 317.933	0.0292584	0		Sb 217.582	0.0652758	0
Cd 214.440	0.0421092	0		Se 196.026	-0.251686	0
Cd 226.502	0.114995	0		Se 203.985	-0.0444721	0.560889
Cd 228.802	0.00861609	0		Si 251.611	-0.0567202	6.41964
Ce 413.380	0.204986	0		Si 252.851	-1.74822	0
Ce 413.764	0.077094	0		Si 288.158	0	0
Ce 418.660	0.0198693	0		Sn 189.927	0.0107729	0
Co 228.616	0.0303842	0		Sn 235.485	264.964	0
Co 230.786	0.252578	0		Sr 407.771	0	0
Co 238.892	2.2886	0		Sr 421.552	0.00130273	0
Cr 205.560	0.0211736	0		Sr 460.733	0	0
Cr 267.716	-0.0469371	0.0942878		Ti 334.940	0	0
Cr 283.563	0.534546	0		Ti 336.121	-0.00203933	0
Cu 224.700	0.262766	0		Ti 337.279	0	0
Cu 324.752	0.0057082	0		Tl 190.801	-0.0526906	0.581942
Cu 327.393	0	0		Tl 276.787	0.584239	9.54736
Fe 238.204	0	0		Tl 351.924	0.0161885	0
Fe 239.562	0	0.392311		V 292.402	0.0449877	-0.100739
Fe 259.939	0	0.333783		V 310.230	-0.00598292	0
Fe 273.955	**n/a**	0		V 311.071	0.00203766	0.32627
Li 610.362	0.147818	0		Zn 202.548	0.0243885	0
Li 670.784	0	0		Zn 206.200	0.00206561	0
				Zn 213.857	0.0680722	0
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